

Europa's surface composition and sputter-produced ionosphere

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Abstract. The efficient sputtering and decomposition of Europa's regolith by energetic charged particles produces an atmosphere representative of its surface composition. In addition to O₂ and H₂ from the decomposition of ice, we show that molecules representative of organics and salts will be present in ionic form at levels detectable using an ion mass spectrometer on an orbiting spacecraft. Such an instrument can also measure isotope ratios to determine surface age.

Introduction

It has been twenty years since the papers by Brown et al. [1978] and Lanzerotti et al. [1978] showed that energetic ions in the jovian magnetosphere efficiently sputter the surfaces of the icy satellites. Europa is now known to have a thin O₂ atmosphere [Hall et al., 1995], which is produced by the sputtering of the satellite's icy regolith by energetic magnetospheric ions [Ip et al., 1998; Saur et al., 1998]. The existence of such an atmosphere was predicted [e. g., Johnson, 1990] based on laboratory studies of ion bombardment of ice [Brown et al., 1982]. Such studies showed that, in addition to H₂O, the ejecta contained stable decomposition products, H₂ and O₂. While the ejected H₂ is readily lost to space, the H₂O and O₂ are not. Whereas the H₂O sticks to the surface [Smith and Kay, 1997], the adsorption time for O₂ is very short, making O₂ the dominant atmospheric species [e. g., Johnson, 1990].

Since the principal sputtering agents at Europa are energetic (100's of keV) S and O plasma torus ions, the yields are large: >10² H₂O molecules per incident ion [e. g., Johnson, 1990]. Therefore, trace volatiles present in the ice or transiently adsorbed on the surface, such as SO₂ [Lane et al., 1982] and, possibly, CO₂ [McCord et al., 1998a], will be carried off with the ejecta. More refractory species, such as sodium salts and organics, will also be sputtered. Therefore, representative molecules will be present in Europa's atmosphere and ionosphere; their detection could confirm the existence of organics and salts from a sub-surface ocean.

Determination of surface composition through the measurement of sputtered material is a standard laboratory technique known as secondary ion mass spectrometry (SIMS). In SIMS, the surface is exposed to a beam of heavy ions and the sputtered ions are detected. At Europa, the impacting heavy ions are provided by the jovian magnetosphere. The possibility of measuring sputter products with spacecraft-borne spectrometers has been suggested for Saturn's icy satellites [Johnson and Sittler, 1990] and the lunar regolith [Elphic et al., 1991]. The yields at Europa will be much larger than those for the Saturnian satellites

and enormous compared to the yields (<0.1 atoms/incident ion) from the sputtering of the lunar surface by solar wind ions [Johnson & Baragiola, 1991].

In this Letter, we estimate ion densities vs. altitude for selected sputter products potentially present in Europa's atmosphere and ionosphere. Even at very small concentrations molecules indicative of organics and ocean salts can be detected using a mass spectrometer on a Europa probe. We first discuss the sputtering and irradiation-induced decomposition of organics and salts and then the preferential loss of sputtered hydrogen.

Europa's Surface Composition

The principal reason for the proposed Europa probe is the possibility of a sub-surface ocean and the existence of prebiotic organic molecules. Although Europa's surface consists predominantly of water ice, non-ice material is known to be present [Calvin et al., 1995]. Prior to the Galileo data on the spectral features of Europa's surface, the only non-water-ice materials to have been identified with reasonable certainty were sulfur, as SO₂ [Lane et al., 1981] and, possibly, polymerized [Johnson et al., 1988; Calvin et al., 1995], and sodium [Brown and Hill, 1996]. Based on near-infrared spectral data acquired with the Galileo NIMS instrument, hydrated salts, predicted by Fanale et al. [1977] and Kargel [1991], and carbon dioxide have been tentatively identified as well [McCord et al., 1998a,b]. In addition, volatiles such as CO, CH₄, and NH₃ [Brown et al., 1988], silicates [Buratti and Golombek, 1988], and organics [Reynolds et al., 1987] have been suggested. In Table 1 are given estimated sputter yields and typical ejected molecules.

Organics. Laboratory studies of the desorption of organic molecules by energetic ion bombardment [e. g., Johnson and Sundqvist, 1992] indicate that, in addition to smaller and more volatile fragment molecules, heavy ion bombardment of organic samples leads to the ejection of large, whole molecules. This is illustrated in Figure 1 for a SIMS study of the amino acid cysteine [Benninghoven et al., 1987]. The incident ions are 45 keV Ar⁺, which have energy deposition profiles comparable to those of jovian energetic S and O ions. Evident in the spectrum are strong peaks corresponding to fragment ions such as HCN⁺, and peaks for CO₂⁺ and the whole molecule minus CO₂. Most interesting is the large signal for the protonated, whole cysteine molecule (mass 122). In addition, corresponding neutral molecules are ejected. Information on the dominant neutrals produced by the sputtering of amino acids such as cysteine is limited; however, the ratio of neutrals to ions can be as large as ~1000 to 1. For hydrocarbons, the dominant neutral products are CH₄ and C₂H_x [e.g., Strazzulla, 1998], while chain molecules (e.g., polymerized formaldehyde [Moore and Tanabé, 1990]) can yield large fragments.

Whereas heavy ion bombardment can sputter large organic molecules as well as smaller fragments such as CO₂ (Figure 1), H⁺, electrons, and UV irradiation cause the decomposition of organic material to considerable depths. CO is a primary

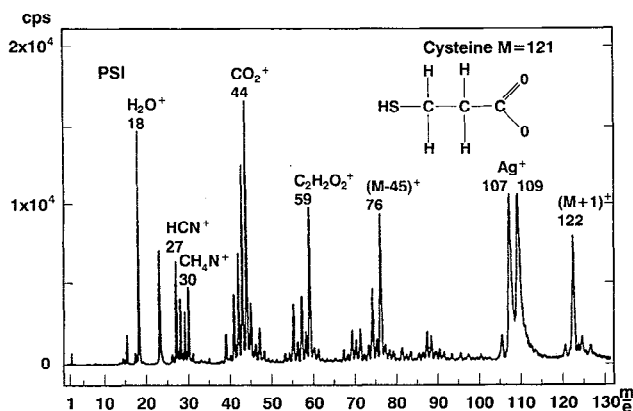


Figure 1. Mass spectrum of ions produced by bombarding a sample of the amino acid cysteine (mass 121 amu) with 45-keV Ar^+ ions: energy deposition rate comparable to that of the energetic S^+ and O^+ that bombard Europa. In addition to the characteristic fragment peaks (e. g., HCN^+ , CO_2^+ , etc.), there is a strong signal for the whole molecule (protonated cysteine, mass 122) [Benninghoven and Sichtermann, 1977; Benninghoven et al., 1987]. If present on the surface of Europa, whole organic molecules may be detectable with an orbiter-borne mass spectrometer. (Figure from Benninghoven, A., and W.K. Sichtermann, Secondary ion mass spectrometry: A new analytic technique for biologically important compounds, *Organic Mass Spectrometry*, 12, 595, 1977. Copyright John Wiley & Sons Limited. Reproduced with permission.)

decomposition product, as well as HCO and HCN [e.g., Calvert and Pitts, 1966; Delitsky and Lane, 1997]. On an oxidizing surface such as Europa's (see below), the CO produced will react with OH or O to become CO_2 . Ion bombardment of the CO_2 thus produced can lead either to the ejection of CO_2 (and its fragments, CO and O_2) or to its destruction and recycling to form new species [e.g., Strazzulla, 1998; Delitsky and Lane, 1997]. In a water-ice surface, ion bombardment causes CO_2 to react with water to form monomeric [Pirronello et al., 1982] or polymerized [Moore and Tanabe, 1990] formaldehyde and an H_2CO_3 residue [Bruccato et al., 1997]. Irradiation-produced carbon suboxide [Chrissey et al., 1989] with adsorbed H_2O can similarly yield H_2CO [Haring et al., 1983].

If organics are present in Europa's surface ice, representative whole organic molecules, small and large fragments, and stable decomposition products will be sputtered into Europa's atmosphere. Therefore, the CO_2 observed in the surfaces of the icy Galilean satellites [McCord et al., 1998a], and in the gas phase at Callisto [R. W. Carlson et al., unpublished data, 1998], may be a decomposition product. Its detection, therefore, may be indicative of the presence of organic molecules. To confirm this, the detection of related species is required.

Salts. The presence of salts on the surface of Europa is suggested by spectral features in Galileo NIMS data that roughly match the spectra of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and their mixtures [McCord et al., 1998b]. If confirmed, this supports the suggestion that hydrated salts, such as $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, would be deposited on Europa's surface in cryovolcanic flows from a subsurface brine ocean [Kargel, 1991]. Laboratory data on the sputtering of salts is limited. Although Wiens et al. [1997] studied Na_2SO_4 , most relevant studies have been on nitrates [Hennig et al., 1953; Knutsen and Orlando, 1997] and alkali-halides, with almost none dealing with hydrated salts. However, from these studies, as well as studies of other sodium-bearing materials [Chrissey et al., 1988], we can infer the ejecta from hydrated salts exposed to energetic ions. The primary

sputter product will be H_2O , because it is most easily removed [P. Williams, unpublished results, 1998]. O_2 is also a decomposition product of salts [Hennig et al., 1953], as are CO or CO_2 (from carbonates) and SO_2 (from sulfates) [Benninghoven, 1969]. Na, Mg, and K (if present) will be sputtered as atoms or molecules (e. g., Na_2O , NaS , NaSO , MgO , etc.).

The presence of sodium on the surface of Europa was inferred from its detection in Europa's atmosphere [Brown and Hill, 1996]. They suggest that sodium is transported from Io in the form of energetic ions, implanted into the surface of Europa, and then sputtered to form a tenuous neutral sodium atmosphere. Implanted sodium would most likely be present as NaOH , which could react in the presence of the radiation flux with SO_2 inclusions in the ice to produce hydrated Na_2SO_4 . Sodium sulfate produced in this manner would be present only in small amounts and would be spatially distributed according to the implantation flux. The proposed implantation scenario is attractive and roughly consistent with the observed abundance of sodium, but, as Brown and Hill note, the sodium sputtered into Europa's atmosphere may have an endogenous source as well as. The Galileo NIMS data [McCord et al., 1998b] suggest surface deposits of Na-containing carbonates from a subsurface ocean brine as a possible endogenous source. Similarly, decomposition of sulfate evaporites as a result of ion bombardment may represent an additional source for the SO_2 observed on Europa [Kargel, 1996].

Oxidizing Surface and D/H Ratio. The preferential loss of H_2 sputtered from Europa's water-ice regolith implies that the satellite's surface is slightly oxidizing [Johnson, 1990; Johnson and Quickenden, 1997]. For this reason, SO_2 rather than H_2S or H_2SO_4 is the species produced by implantation of sulfur ions [Johnson et al., 1988]. An oxidizing surface suggests that hydrocarbons will not be prevalent and, further, that certain decomposition pathways for organics and salts will be enhanced. In the case of sulfate salts, for example, the following decomposition pathways are favored in an oxidizing environment: $\text{MgSO}_4 + \text{O} \rightarrow \text{MgO} + \text{SO}_2 + \text{O}_2$ and $\text{MgSO}_4 + \text{OH} \rightarrow \text{MgOH} + \text{SO}_2 + \text{O}_2$; and $\text{Na}_2\text{SO}_4 + \text{O} \rightarrow \text{Na}_2\text{O} + \text{SO}_2 + \text{O}_2$ and $\text{Na}_2\text{SO}_4 + 2\text{OH} \rightarrow 2\text{NaOH} + \text{SO}_2 + \text{O}_2$. Here, as in the case of water ice, the most volatile decomposition products (e.g., SO_2 , O_2 , Na) will be preferentially sputtered. Thus, we expect MgO , MgOH , Na_2O , and NaOH to be among the species sputtered from Europa's surface if salts are present in sufficient abundance. As stated above, CO_2 will be produced from organics and carbonates, directly or following production of CO .

Because of the preferential loss of hydrogen and the mass difference between H and D, Europa's surface will be enriched in D relative to H [Johnson, 1990; Johnson and Quickenden, 1997]. Measurement of the D/H ratio, together with modeling, can provide an important constraint on the lifetime of Europa's surface materials. In addition, its difference from that in the flux of incident magnetospheric ions can provide information about the importance of Europa as a source of hydrogen for the jovian magnetosphere.

Potential Atmospheric /Ionospheric Constituents

The peak of the sputter flux occurs at $\sim 500\text{keV}$ S^+ and O^+ [Cooper et al., unpublished results, 1998]. Table 1 shows yields produced by such ions for solids made up of each molecular species. These should only be used as guides, since the molecules present at Europa may be hydrated or mixed into the water-ice matrix. At the temperatures on Europa, ice can trap even the most volatile species, if it is present in small concentrations [Hudson and Donn, 1991]. Therefore, to obtain atmospheric concentrations we assume the volatiles and organics are carried off with ice. We

Table 1. Sputtering yields and decomposition products for bombardment by 500 keV S⁺ and O⁺

Material	Yield/Ion	Ejecta
H ₂ O (18 amu) (a)	200-300	H ₂ O, H ₂ , O ₂
SO ₂ (64 amu) (a)	400-600	SO ₂ , SO, O ₂
NH ₃ (17 amu) (a)	600-900	NH ₃ , H ₂ , N ₂
CO ₂ (44 amu) (a)	800-1200	CO ₂ , CO, O ₂
Glycerol (92 amu) (b)	~50	
POM (30 amu) (c)	~4	CO, HCO, H ₂ CO, CO ₂ , (H ₂ CO) ₂ , etc.
L-Leucine (131 amu) (d)	>~2	Leucine+volatiles
Na ₂ SO ₄ ·XH ₂ O (c,f,g)	~0.5	Na, O ₂ , NaO, Na ₂ O, Na ₂ , NaS, SO ₂ , NaSO
SiO ₂ (60 amu) (h)	0.4-1	SiO, O ₂ , Si

(a) Johnson [1990; 1998]; (b) Williams & Gillen [1989]; (c) Moore & Tanabe [1990]; (d) Eriksen et al., [1997]; (e) Chrissey et al., [1988]; (f) Wiens et al., [1997]; (g) Hennig et al., [1953]; and (h) Betz & Wehner [1985].

scale the atmospheric concentration to that measured for O₂, assuming [O₂] = 10¹⁵ cm⁻² [Hall et al., 1996]. With a neutral scale height on the order of 100 km [Kliore et al., 1997], this gives a surface density, n_{O2} = 10⁸ cm⁻³. These values are roughly consistent with recent modeling results [Ip et al., 1998; Saur et al., 1998].

Neutral densities were derived in two ways. Volatiles with short residence times such as NH₃ and SO₂ are scaled as 1% of the O₂ column density, and the altitude dependence up to 250 km is given by $n(z) = n_0 \exp(-z/H)$, where z is the altitude, $H = (M_{O2}/M)100$ km, and M is the molecule's mass. Since O₂ itself is ~10-30% of the sputter ejecta from ice, we are assuming small concentrations (~0.1-0.3%) of these molecules in an ice matrix.

For sputtered species that stick with long residence times when they return to the surface (e.g., salts and organics), we scale to the sputter-produced H₂O column density. We assume that [H₂O] = 5 × 10¹³/cm⁻² [Johnson, 1990] and scale the non-volatile sputter products as 1% of the H₂O column. Since cysteine is a large molecule, although the average yield is significant (e.g., leucine Table 1), only the larger sputter ejection events will carry off whole molecules. In addition, it may be susceptible to fragmentation. Therefore, we scale it to 0.1% of H₂O in order to estimate detectability. Although there may be some collisions in the atmosphere, these species will have no surface-equilibrated component. Thus, we use the height dependence for a sputter-produced atmosphere close to the surface, $n(z) = n_0 [1 + (z/H_c)]^{-3/2}$ [Johnson, 1990; Eq. 4.19a]. Using the data for the sputtering of ice by 45 keV Ar⁺ [e.g., Johnson, 1990; Fig. 3.24] for the sputter scale height, we obtain $H_c = 0.055 \text{ eV/Mg}$, where g is Europa's surface gravity 145.5 cm s⁻².

In contrast, the atmospheric Na observed at ~5 R_E [Brown and Hill, 1996] is primarily the escaping component reduced at larger distances by ionization. A lower bound on the surface density, ~200 Na cm⁻³, is obtained using the expressions for a sputter-produced atmosphere [Johnson, 1990; Eqs. 4D.1, 4D.2]. This is larger than our estimated surface NaSO density. In addition, the surface flux for each trace molecule consistent with the above approximations is conservative, as it is less than the flux obtained using the incident ion flux and the yields in Table 1.

The sputtered trace constituents of the atmosphere are most sensitively detected by measuring their ions. For local equilibrium in the ionosphere over the altitude region of interest, $n(\text{ion})/n(\text{neutral}) = \tau_L/\tau_i$, since $n(\text{ion}) = [dn(\text{neutral})/dt]\tau_L$ and $[dn(\text{neutral})/dt] \approx [n(\text{neutral})/\tau_i]$, where τ_i is the lifetime against ionization and τ_L is the ion loss time. Whereas ions are lost by

recombination and plasma flow, they are produced by electron impact, charge exchange with the dominant ion, and photo-ionization [Kliore et al., 1997; Ip et al., 1998; Saur et al., 1998]. For charge exchange rates and to determine τ_L we assume that the total ionospheric density near the surface is 10⁴ cm⁻³. Since the loss is likely to result from ion-convection [Ip et al., 1998; Saur et al., 1998], τ_L is roughly the same for all ions. In the O₂ atmosphere electron cooling is efficient at the densities indicated above. Therefore, although the electrons certainly contribute to the ionization, the contribution from electron-impact ionization is uncertain. Therefore, we scale to the measured ionosphere using only the photo-ionization rate [Huebner et al., 1992, Table 2] and rate of charge transfer with dominant ion [Anicich, 1993], presumed to be O₂⁺, to obtain τ_i for each ion considered.

In Fig. 2 the ion density vs. altitude is given for each molecular ion using the estimates for neutral densities above and a τ_i/τ_L that is independent of z . These results can be used to scale the ion densities when better values for the neutral densities are obtained. In addition, ion densities can be much larger in the flanks of the plasma flow around Europa. Modern time of flight mass spectrometers are sensitive to masses much larger than cysteine, can detect densities ~10⁻³ cm⁻³, and have excellent mass resolution. Therefore, from Fig. 2 we show that, even for the small concentrations assumed, all the molecular ions presumed to be present can be detected by an ion-mass spectrometer operating in the orbital range (~30-200 km) of a Europa probe. In addition, since the collisional mean free path is < ~100 km near the surface, spatial resolution of sources is

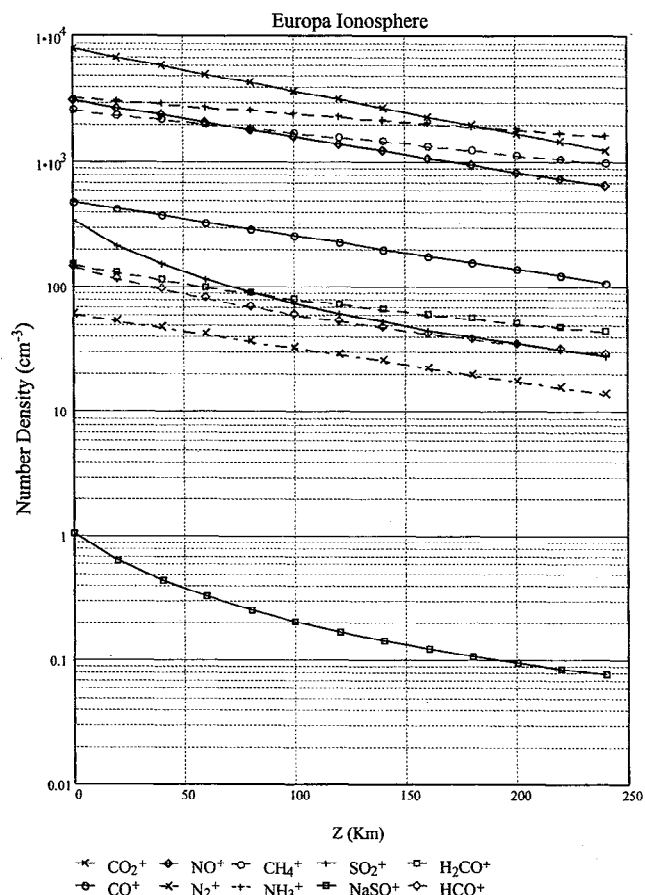


Figure 2. Ionospheric densities vs altitude, determined as discussed in the text, for molecules sputtered from the surface due to the presence of suggested surface materials. All densities exceed the detection limit (10⁻³ cm⁻³) of a modern time of flight mass spectrometer such as the Cassini Plasma Spectrometer.

possible in the lower orbits (30 - 200 km) for the interesting non-volatile molecules.

Conclusions

Europa is the subject of intense scrutiny because it may have a sub-surface ocean that brings organic materials to the surface through faults and fissure. To confirm these exciting possibilities, the Europa Probe is slated to be the first of NASA's outer solar system (Fire and Ice) missions. In this paper we have shown that because sputtering by the energetic S^+ and O^+ is very efficient the plasma flux from the jovian torus, which produces the observed atmospheric species O_2 and Na, will also produce other atmospheric components characteristic of the surface composition. This provides the exciting possibility of remotely sampling components representative of salts from a sub-surface ocean and organic molecules possibly indicative of prebiotic activity. We also point out that the observed species, Na, SO_2 , and CO_2 , may already indicate the presence of such materials. Although additional molecular identifications may be obtained from telescopic and Galileo spectra, our results show that very small concentrations of these molecules and their decomposition products can be detected with a mass spectrometer on the proposed Europa probe.

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